

# UNIFORM DROPLET DEPOSITION OF THICKENED CHEMICAL AGENT SIMULANTS BY SUPERCRITICAL CARBON DIOXIDE VISCOSITY REDUCTION

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## ABSTRACT

Study of the fate of chemicals on substrates requires that those chemicals be applied to the substrate in a uniform and reproducible manner. Relatively simple means of droplet deposition of non-viscous chemicals are satisfactory, however thickened chemicals present problems using the same deposition techniques. By using supercritical carbon dioxide as a diluent, we were able to reduce the viscosity of various polymer-thickened chemicals and store them in a high-pressure reservoir. We achieved up to 20 fold reductions in viscosity of polymer-chemical mixtures and deposit them with no residual solvent retained within the deposited material.

## INTRODUCTION

Study of the fate of chemical agent simulants on various substrates requires that those agents be applied to the substrate in a uniform and reproducible manner<sup>1</sup>. Relatively simple means of droplet deposition for neat simulants are satisfactory, however thickened simulants present problems using the same deposition techniques. Sessile droplets ranging from 0.5mm to 5.0mm in diameter are desirable for simulation of actual deposition of chemical warfare agents on the ground and surfaces of equipment. Due to their high viscosity and non-Newtonian rheology, thickened simulants produce irregular sized droplets and filaments that upset the uniformity of deposition. Previous attempts to spray a thickened simulant using a pressurized stream produced random patterns of globular drops and strings.<sup>2</sup>

Supercritical fluids are formed when a liquid is heated and compressed above its critical point (31.1°C and 73.8 bar). The density of a supercritical fluid approaches that of a liquid but in addition displays the diffusibility of a gas. High molecular weight compounds can be dissolved by supercritical fluid alone or by modifying the supercritical fluid with another compound called a “modifier”. Near-supercritical fluids, liquids at a point just below their critical pressure, and above their critical temperature, also display similar solubility and diffusion characteristics as supercritical fluids.

A preliminary investigation into the mechanisms affecting the dissolution of polymers by supercritical fluids was undertaken to identify methods available and obstacles to be avoided.

It was thought that an enclosed, pressurized stream of supercritical CO<sub>2</sub> (ScCO<sub>2</sub>) could be used to mobilize a polymer thickened chemical simulant and controllably deposit (droplet size and distribution) it on a selected substrate. A ScCO<sub>2</sub> method for the dissolution of poly methyl methacrylate (PMMA) was first evaluated. A ScCO<sub>2</sub> micro extraction apparatus (Suprex® Prepmaster®) was used to attempt the dissolution of PMMA. The result was that although the PMMA could be transitioned to a swollen glassy mass, dissolution could not be accomplished.

Report Documentation Page				Form Approved OMB No. 0704-0188	
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1. REPORT DATE <b>16 NOV 2004</b>		2. REPORT TYPE <b>N/A</b>		3. DATES COVERED <b>-</b>	
4. TITLE AND SUBTITLE <b>Uniform Droplet Deposition Of Thickened Chemical Agent Simulants By Supercritical Carbon Dioxide Viscosity Reduction</b>				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) <b>AFRL/MLQL, 139 Barnes Dr., Suite 2, Tyndall AFB, FL 32403</b>				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT <b>Approved for public release, distribution unlimited</b>					
13. SUPPLEMENTARY NOTES <b>See also ADM001849, 2004 Scientific Conference on Chemical and Biological Defense Research. Held in Hunt Valley, Maryland on 15-17 November 2004 .</b>					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT <b>UU</b>	18. NUMBER OF PAGES <b>7</b>	19a. NAME OF RESPONSIBLE PERSON
a. REPORT <b>unclassified</b>	b. ABSTRACT <b>unclassified</b>	c. THIS PAGE <b>unclassified</b>			

Next, the addition of methanol as a “modifier” was added to the  $\text{ScCO}_2$ , in order to facilitate the dissolution of the PMMA. The results were more promising than using  $\text{ScCO}_2$  alone because a spongy viscous mass was produced, however, no dissolution was observed. A thickened mixture of PMMA and dimethyl malonate was entrained into a stream of  $\text{ScCO}_2$ . The  $\text{ScCO}_2$  extracted the dimethyl malonate from the PMMA resulting in phase separation.

Finally, a shift in the philosophy of incorporating the thickened simulant into a stream of  $\text{ScCO}_2$  that could be sprayed was amended to that of mixing  $\text{ScCO}_2$  into the thickened simulant producing a less viscous solution that could be sprayed much like paint.

$\text{ScCO}_2$  was used previously to reduce the viscosity of concentrated paints for spray deposition.  $\text{ScCO}_2$  replaces the organic solvents traditionally used for viscosity reduction and minimizes the volatile organic compounds released into the atmosphere. Various U.S. Patent's have been granted for this process to Union Carbide and Plastics Company Inc<sup>3</sup>. A thickened simulant is formulated in much the same way as paint. Paint's polymeric system is dissolved in a thinner or vehicle such as xylene to form a low viscosity fluid that has the ability to be sprayed, a thickened simulant's polymeric system is also dissolved in a thinner but in this case it is the simulant. We proposed that  $\text{ScCO}_2$  could be used to reduce the viscosity of a thickened simulant and could facilitate the deposit of a uniform size droplet of a thickened simulant on an appropriate substrate.

Aerodynamic breakup of Newtonian liquids emanating from a spray nozzle is well understood. Uniform droplets form within a defined size distribution, given pressure and orifice dimensions. Visco-elastic (non-Newtonian) liquids by contrast produce irregular droplets making pattern prediction difficult.

Study of the physiochemical fate of a simulant that has been thickened requires that the physical properties of the thickened simulant mix be not altered during application to the chosen substrate. The use of  $\text{ScCO}_2$  as a viscosity reducer is well suited because shortly after deposition the thickened simulant returns to atmospheric pressure and ambient temperature with rapid evaporation of  $\text{CO}_2$ .

## EXPERIMENTAL

**APPARATUS:** A 100ml internal volume, stirred reaction cell (Thar Technologies, Inc.), fitted with two, ½ inch diameter sapphire windows, was used to mix, observe phase changes and retain the thickened simulants. Phase changes were observed and recorded using a Panasonic© digital video camera. Supercritical carbon dioxide was produced in a custom designed supercritical  $\text{CO}_2$  system composed of control computer, high-pressure pump, pressure regulators and temperature control (Thar Technologies, Inc.), which are shown in Figures 1 and 2.



FIGURE 1. Reaction cell.



FIGURE 2. Pump system.

Supercritical carbon dioxide was transferred from the pump system to the reaction cell and from the cell to the spray gun through ⅛" O.D. x 0.049" wall thickness, stainless steel tubing. The reaction cell was wrapped with 120v heating tape and temperature controlled by a temperature controller (Valco® model

ITC10399, 0-100°C). Relative viscosity measurements were performed using a falling needle style high-pressure viscometer fabricated and calibrated in-house. The viscometer was constructed using  $\frac{3}{8}$ " O.D. x 0.049" wall thickness, stainless steel tubing. The tube was terminated on both ends with stainless steel nuts to facilitate coupling with the reaction cell (Swagelok® SS-602-1). Battery powered Hall Effect switches attached to light emitting diodes (LED), were used to detect passage of an aluminum needle encasing a rare earth magnet. Viscosity measurements were obtained by timing the fall time of the needle between the Hall switches. Calibration was performed with certified standards (Cannon Standards®) 15-900 centipoise (cP) at 1700 psig, using the linear regression of fall times of the calibration standards. Reduced viscosity thickened simulant was sprayed through a heated, high speed, high-pressure automatic spray gun (AutoJet® model 26AUH, Spraying Systems Co.®). The nozzle was fitted with a 0.008-inch diameter orifice modified by installing a narrow bore stainless steel tube and filling with epoxy resin, shown in Figure 3. Deposition dwell time was controlled by a solid state timing control (AutoJet® model 1250, Spraying Systems Co.®).

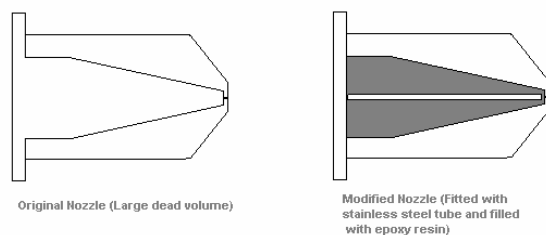


FIGURE 3. Modified nozzle.

**MATERIALS:** Polymers used to thicken simulants were Paraloid® K125 manufactured and provided by Rhom and Haas, Co. Three simulants were evaluated with varying degrees of polymer solubility to evaluate the robustness of the process. Diethyl malonate (DEM) 99%, Aldrich, dibutyl malonate (DBM) 99+%, Aldrich, and tributyl phosphate (TBP) 99%, Eastman Co. were chosen. DEM and DBM were evaluated with Paraloid® K125. Liquid carbon dioxide was obtained from Airgas, USA and weight determinations were performed on a Mettler® AE160 laboratory balance.

**PRELIMINARY EXPERIMENTATION:** To establish research direction and validate the proposed hypothesis a small scale ScCO<sub>2</sub> apparatus was constructed to explore the solvency of ScCO<sub>2</sub> on Paraloid® K125. It was immediately found that ScCO<sub>2</sub> alone could not dissolve the polymer. Only after dissolution of the polymer in the simulant could ScCO<sub>2</sub> further reduce the viscosity of the mixture, in effect the simulant acts as a modifier. Simulants thickened with their respective thickener would be used as starting mixtures in all subsequent experimentation.

**VISCOSITY REDUCTION:** Thickened simulants of various compositions were placed in the reaction cell heated to 40°C. The cell was then brought to the tank pressure of liquid CO<sub>2</sub>. Using the pump system, varying amounts of CO<sub>2</sub> were introduced into the reaction cell increasing the pressure to 77-80 bar depending on the amount of CO<sub>2</sub> added. Continuous mixing of the polymer / simulant was accomplished by use of the in-cell stirrer. The viscosities of the resulting mixtures were measured and plotted versus the CO<sub>2</sub> concentration. A target viscosity of 35 cP was selected as the research goal because of spray gun manufacture recommendations.

**THICKENED SIMULANT DEPOSITION:** After viscosity measurements were performed, the viscometer was replaced by the high-pressure spray gun. The gun, controlled by a precision timer, is

actuated by energizing a solenoid valve. A tungsten carbide ball valve is momentarily lifted from its seat allowing the pressurized fluid to flow into the nozzle. Once the CO<sub>2</sub> entrained fluid leaves the nozzle, the CO<sub>2</sub> returns to the gaseous state, releasing energy that breaks the fluid into small droplets. The nozzle, designed to produce a zero degree solid stream, directs the fluid to the target surface. Upon impact, the remaining CO<sub>2</sub> flashes away, leaving the thickened simulant behind as shown in Figure 4. The target for the experimental deposition of thickened simulant was chosen to be a 25mm round filter, LS 50um pore size (Millipore Corp.).

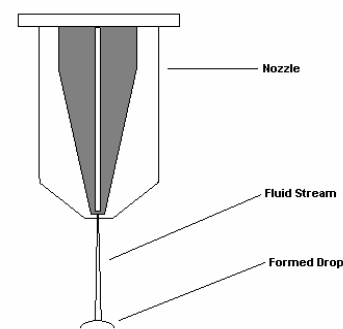


FIGURE 4. Simulant deposition.

## RESULTS

**VISCOSITY REDUCTION:** Several simulant vs. thickener combinations were evaluated to show that viscosity reduction was not unique to any one system. CO<sub>2</sub> concentrations were calculated by dividing the weight of experimentally added CO<sub>2</sub> by the sum of the weights of the thickened material in the cell and the weight of CO<sub>2</sub> added in grams, times 100.

**THICKENED DIBUTYL MALONATE:** Initially viscosity reduction of thickened dibutyl malonate (DBM) at 4% w/w was investigated at seven different CO<sub>2</sub> concentrations. Reference viscosity of thickened DBM (4% w/w) at room temperature (23°C) and 0% CO<sub>2</sub>, was determined to be 580 centipoise (cP). Table 1 and Figure 5 display the viscosity reduction at increasing CO<sub>2</sub> concentrations. At a CO<sub>2</sub> concentration of 46% (37 gm), the viscosity was reduced to approximately 25 cP at 40°C demonstrating proof of concept.

TABLE 1. Viscosity reduction of Paraloid® K125 (4% w/w) thickened DBM

<i>CO<sub>2</sub> Concentration (% w/w)</i>	<i>Temperature (°C)</i>	<i>Viscosity (cP) (± 1 S.D.)</i>
0	23	580 ± 8
0	40	305 ± 11
11	40	140 ± 4
22	40	71 ± 2
32	40	50 ± 2
37	40	39 ± 2
41	40	32 ± 1
46	40	25 ± 1

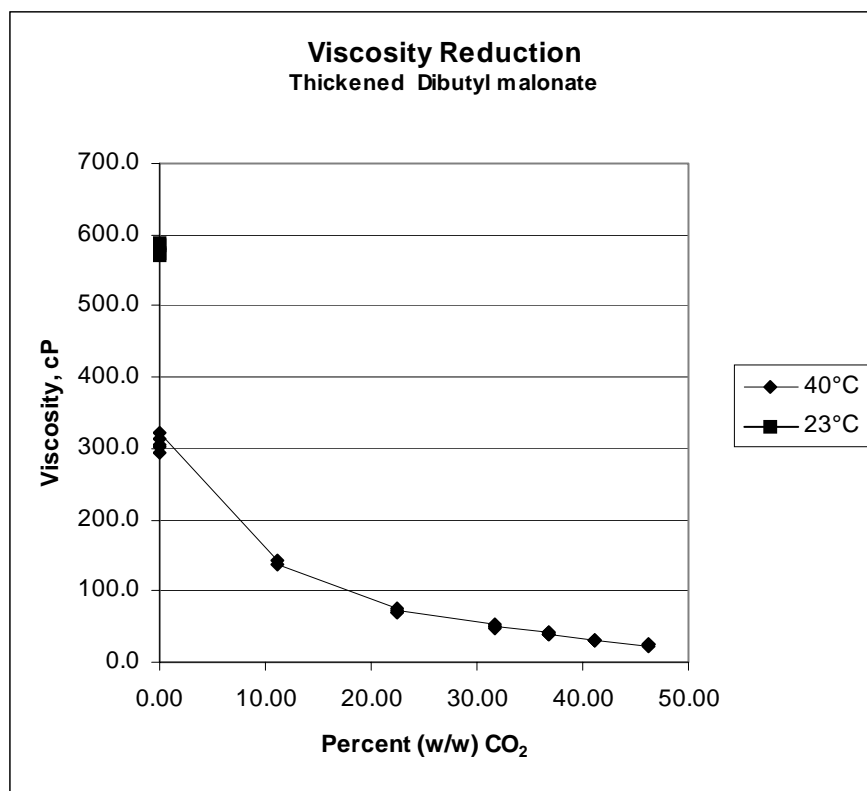


FIGURE 5. Viscosity reduction of Paraloid® K125 (4% w/w) thickened DBM.

THICKENED DIETHYL MALONATE: Diethyl malonate (DEM) thickened with 4% (w/w) Paraloid® K125 was evaluated at multiple CO<sub>2</sub> concentrations and temperatures. Figure 6 shows the effect of increasing CO<sub>2</sub> concentrations versus temperature on the viscosity of the thickened DEM. During these experiments, it was noted that the lower viscosity limit was reached at 15cP on the 26% (w/w) CO<sub>2</sub> concentration curve, and additional CO<sub>2</sub> produced no additional viscosity reduction. The target viscosity of 35cP was easily attained. Table 2 summarizes the data collected.

TABLE 2. Viscosity reduction of Paraloid® K125 (4% w/w) thickened DEM

CO <sub>2</sub> concentration (% w/w)	Temperature (°C)	Viscosity (cP) (± 1 S.D.)
0	21	189 ± 2
0	31	156 ± 7
0	41	130 ± 2
0	45	114 ± 1
8.5	21	50 ± 1
8.5	26	48 ± 1
8.5	30	44 ± 3
8.5	35	41 ± 1
8.5	42	38 ± 1
8.5	45	37 ± 1
8.5	54	29 ± 1
15	25	26 ± 2
15	32	22 ± 1
15	39	19 ± 1
15	45	16 ± 1
15	49	15 ± 1
15	59	13 ± 2
21	29	17 ± 1
21	44	13 ± 1
21	47	13 ± 1
21	55	14 ± 2
26	35	13 ± 1
26	44	12 ± 1
26	51	15 ± 1

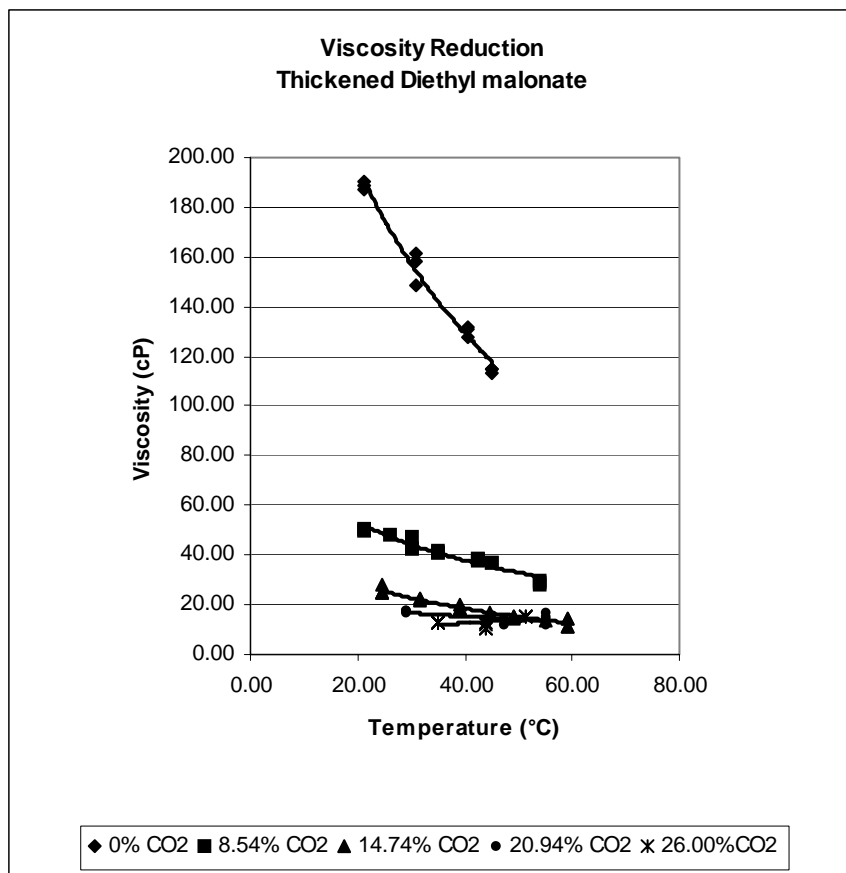


FIGURE 6. Viscosity reduction of Paraloid® K125 (4% w/w) thickened diethyl malonate.

## CONCLUSIONS

The use of supercritical CO<sub>2</sub> has been established as a viable means of reducing the viscosity of several thickened chemical agent simulants to a point at which they can be reproducibly sprayed. The fundamental principles are simple and straightforward. Demonstration of a spray deposition technique was accomplished, although sessile droplet diameter of less than 3mm was not possible due to physical limitations of the experimental apparatus.

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